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*Research article*

## Optical spectroscopic characterization of amorphous germanium carbide materials obtained by X-Ray Chemical Vapor Deposition

Paola Antoniotti<sup>1</sup>, Paola Benzi<sup>1,2,\*</sup>, Chiara Demaria<sup>1,\*</sup>, Lorenza Operti<sup>1</sup>, and Roberto Rabezzana<sup>1</sup>

<sup>1</sup> Department of Chemistry, NIS Reference Center, University of Torino, via Pietro Giuria 7, 10125 Torino, Italy

<sup>2</sup> INSTM via Giusti, 9, 50121 Firenze, Italy

\* **Correspondence:** Email: paola.benzi@unito.it; chiara.demaria@unito.it; Tel: +39-011-670-7581; Fax: +39-011-670-7591.

**Abstract:** Amorphous germanium carbides have been prepared by X-ray activated Chemical Vapor Deposition from germane/allene systems. The allene percentage and irradiation time (total dose) were correlated to the composition, the structural features, and the optical coefficients of the films, as studied by IR and UV-VIS spectroscopic techniques. The materials composition is found to change depending on both the allene percentage in the mixture and the irradiation time. IR spectroscopy results indicate that the solids consist of randomly bound networks of carbon and germanium atoms with hydrogen atoms terminating all the dangling bonds. Moreover, the elemental analysis results, the absence of both unsaturated bonds and CH<sub>3</sub> groups into the solids and the absence of allene autocondensation reactions products, indicate that polymerization reactions leading to mixed species, containing Ge-C bonds, are favored. E<sub>opt</sub> values around 3.5 eV have been found in most of the cases, and are correlated with C sp<sup>3</sup>-bonding configuration. The B<sup>1/2</sup> value, related to the order degree, has been found to be dependent on solid composition, atoms distribution in the material and hydrogenation degree of carbon atoms.

**Keywords:** germanium carbide; X-Ray activated CVD; optical properties; binary alloys; amorphous materials

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### 1. Introduction

The amorphous alloys, such as Si-C, Si-Ge and Ge-C are very important materials in current technologies and have stimulated a growing interest due to their electrical, optical and structural properties and their low cost compared with that of the crystalline form[1,2] making them suitable for

different applications. They can be prepared by several techniques: materials with composition, and hence properties, varying in a wide range are obtained changing the preparation method, the deposition conditions and/or the precursors [3–31].

In our laboratory, hydrogenated germanium carbides have been produced by X-ray activated - Chemical Vapor Deposition from germane/hydrocarbons systems [32–42] which is an innovative method to obtain materials from decomposition of gaseous reactants. Our previous results indicate that, by changing the hydrocarbon species mixed with germane or the hydrocarbon/germane molar ratio in the mixture, materials in a wide range of composition with different characteristics can be obtained. For GeH<sub>4</sub>/alkane mixtures, the percentage of carbon atoms in the solid increases with the number of carbon atoms in the reactant hydrocarbon molecule but it remains low even when an high hydrocarbon molar fraction in the irradiated mixture is employed. Moreover, an increase of hydrocarbon percentage in the mixture causes a decrease of the solid yield [32–35].

When irradiation of germane takes place in the presence of unsaturated hydrocarbons, the carbon incorporation in the solid during the polymerization reactions sharply increases [36–42] proportionally to the unsaturation degree of the hydrocarbon. Moreover, the bonding and the properties of the materials obtained by radiolysis of mixtures with hydrocarbons having a double bond [36–37] are different from those of the solids obtained using alkynes [38–42].

The solids yield increases if unsaturated hydrocarbons are employed. However, results obtained in previous works using ethene or ethyne [36–42] show that the composition—and hence the properties —of materials are closely affected by irradiation time. The composition of deposited material changes quickly during irradiation making difficult to obtain uniform films.

Here we report the results of studies performed with the aim to obtain materials with constant composition and properties with respect to the irradiation time. Characterization of materials obtained at room temperature by X-ray activation of germane/allene mixtures with different hydrocarbon percentage and increasing irradiation dose is presented.

## 2. Materials and Method

The samples were obtained by X-ray activated Chemical Vapor Deposition technique, using a CPXT-320 tube by Gilardoni SpA, with a maximum output of 320 keV, as X-ray source. The absorbed dose rate of reactant species was about  $5 \times 10^3$  Gy/h. The germane/allene mixtures were irradiated at room temperature in 365 mL Pyrex vessels, at a total pressure of 700 Torr, varying the total irradiation time between 1 and 5 hours. GeH<sub>4</sub>/C<sub>3</sub>H<sub>4</sub> mixtures with 5, 10, 20, 30, 50 and 70% of allene have been irradiated.

Allene (97% purity) and GeH<sub>4</sub> monogermane were supplied by S.I.A.D. (Società Italiana Acetilene e Derivati) S.p.A.

In the synthesis procedure, the vial bottom (with KBr pellets and quartz substrate discs) was positioned on the primary beam trajectory, so that both gaseous molecules and growing solids were activated by the main X-ray beam.

The solid products were collected, weighted and their composition was determined by means of a Thermo Electron Corporation CHNS-O analyzer for H<sub>total</sub> and C content while the Ge content was calculated as the difference.

The products were examined by IR spectroscopy (KBr pellets) with a FTIR Bruker Equinox 55 instrument equipped with a deconvolution program of overlapped peaks. The resolution was  $2\text{ cm}^{-1}$ . All spectra were recorded at room temperature.

The UV-VIS spectra were obtained with a Perkin-Elmer Lambda 15 spectrophotometer from the material deposited on the quartz disk, using a clean quartz disk irradiated at the same dose as a reference. To avoid any possible oxidation by oxygen in the air all the analyses on solids were performed immediately after opening the vials.

### 3. Results and Discussion

$\text{Ge}_x\text{C}_{1-x}\text{H}$  alloys have been prepared by X-Ray Chemical Vapor Deposition (X-Ray CVD) from mixtures of  $\text{GeH}_4$  with allene. The effects of the  $\text{C}_3\text{H}_4$  molar fraction in the irradiating mixture on the solid chemical composition and bonding configuration have been investigated. Samples obtained from radiolysis of mixtures containing 10, 30, 50 and 70% of allene were analyzed. Moreover, since the most evident changes of solids composition are observed if allene percentage lower than 30% is employed, materials obtained after 5 hours irradiation of mixtures with 5 and 20 allene percentage have also been investigated. The irradiation dose effect on the composition, the characteristics and the properties of the deposited solids, has also been verified performing experiments varying the irradiation time from 1 to 5 hours each step.

From the irradiation of germane/allene mixtures, solid products were obtained, which deposited on the bottom of irradiated ampoules. Films were obtained when mixtures with 30% of allene were irradiated. Moreover, films were obtained from mixtures with lower or higher allene percentage for irradiation times higher than 1 hour, independently from the allene percentage, with the exception of the 5% allene mixture which leads to powders deposition after 5 hours irradiation.

It is noteworthy to remind that previously performed experiments on germane alone [43–44] produced a black powder of an amorphous cross-linked polymer whereas at the doses used here, no solid product is formed from irradiation of allene alone. Moreover, a considerably lower quantity of solid is obtained when germane is irradiated alone even if the irradiation time is higher. The experimental results indicate that reactions between  $\text{GeH}_4$  and  $\text{C}_3\text{H}_4$  are greatly favored with respect the self-condensations of the two precursors and indicate that the solids collected are not simple mixture of co-precipitated hydrogenated C-C or Ge-Ge polymers, but instead a network containing Ge-C bonds. At room temperature the solids are stable to the air and insoluble in the common organic solvents. The solids composition has been determined by elemental CHNS-O analysis for H and C content while the Ge content was calculated as the difference.

In Figure 1, the yield percentage (calculated with respect the total precursors mass) of the solid phases obtained from irradiation of the different  $\text{GeH}_4/\text{C}_3\text{H}_4$  mixtures and after different irradiation time are reported. C and H contents are shown in Figures 2 and 3 as carbon molar fraction (defined as  $\text{C}/\text{C}+\text{Ge}$ ) and hydrogenation degree (defined as the atomic ratio  $\text{H}/\text{C}+\text{Ge}$ ), respectively.

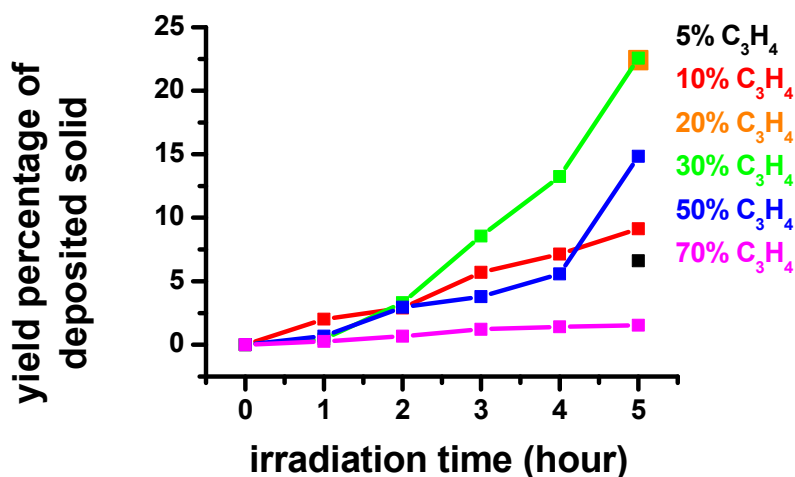


Figure 1. Yield percentage of solids obtained from irradiation of  $GeH_4/C_3H_4$  mixtures with different  $C_3H_4$  percentage as a function of the irradiation time.

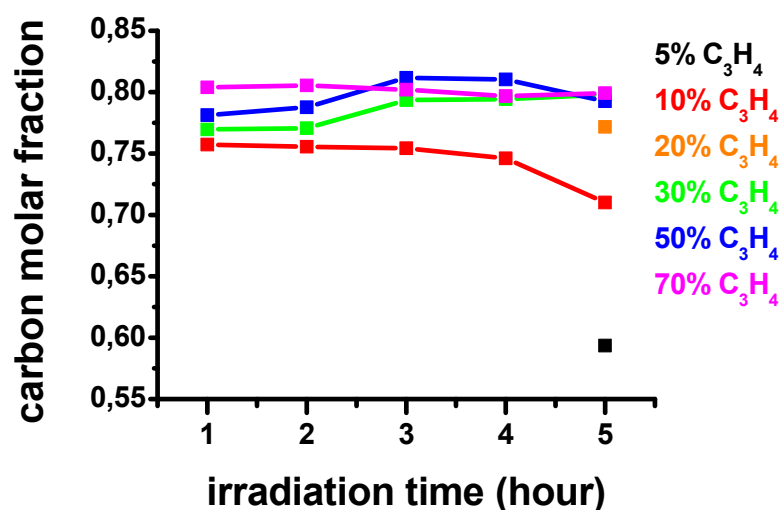
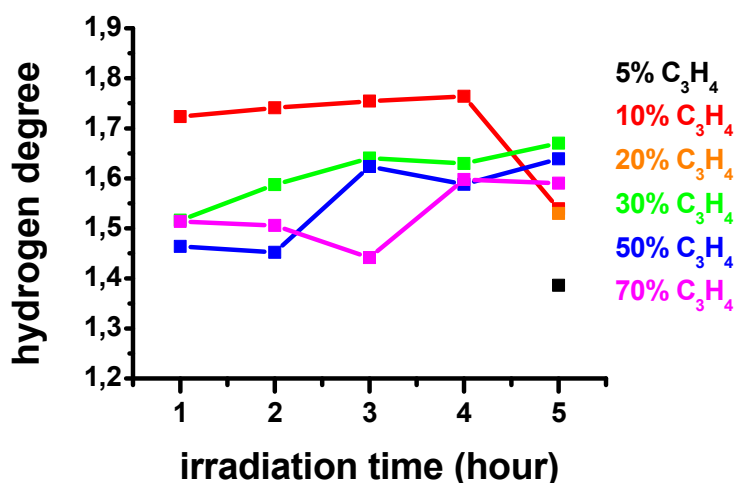


Figure 2. Carbon molar fraction ( $C/C+Ge$ ) ratio of solids obtained from  $GeH_4/C_3H_4$  mixtures with different  $C_3H_4$  percentage and after different irradiation time as a function of the irradiation time.



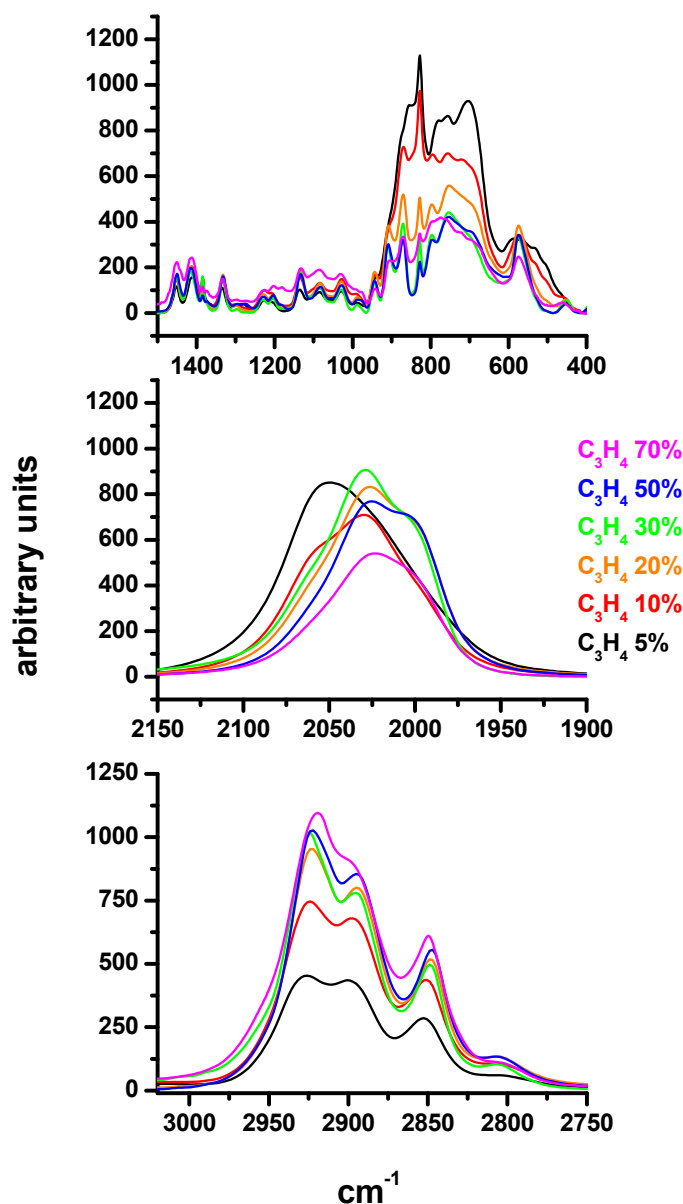
**Figure 3. Hydrogenation degree (H/C+Ge) ratio of solids obtained from irradiation of GeH<sub>4</sub>/C<sub>3</sub>H<sub>4</sub> mixtures with different C<sub>3</sub>H<sub>4</sub> percentage as a function of the irradiation time.**

The solid yields increases with irradiation time (as expected) and little variation of the carbon content is observed for materials obtained from mixtures with the same allene percentage and irradiated for increasing time. Only, the solids obtained from 30% allene mixture exhibit a C/C+Ge ratio increasing up to 5 hours. Moreover, it is interesting to note that the carbon molar fraction varies, for each mixture, in a narrow range with respect to those observed for solids deposited from X-Ray CVD of GeH<sub>4</sub>/C<sub>2</sub>H<sub>2</sub> systems and irradiated for the same time. For example, C/C+Ge ratio values from 0.79 to 0.86 are found for materials from mixtures with 30% of ethyne irradiated for 1 and 2 hours, respectively [40], whereas from the analogous mixture with allene, solids with about the same C/C+Ge ratio are obtained.

IR spectroscopy was used to investigate the structures and the hydrogen bonding configurations of the a-GeC:H materials obtained; these are interesting features because hydrogen can terminate the dangling bonds thus affecting the optical and electrical properties of the materials. In fact, it is known [9,45] that passivation promotes formation of sp<sup>3</sup> hybridized C atoms over the sp<sup>2</sup> ones thus influencing the material disorder degree.

Figure 4 shows the IR spectra of the solids obtained from 5 hours irradiation of mixtures with C<sub>3</sub>H<sub>4</sub> percentage ranging from 5 to 70% while, in Figure 5, the IR spectra of the solids obtained from mixtures with 30% of C<sub>3</sub>H<sub>4</sub> and increasing irradiation time (1–5 hours) are reported as an example. The spectra have been superimposed and divided in three regions: from 3050 to 2750 cm<sup>-1</sup>, from 2150 to 1900 cm<sup>-1</sup> and from 1500 to 400 cm<sup>-1</sup>.

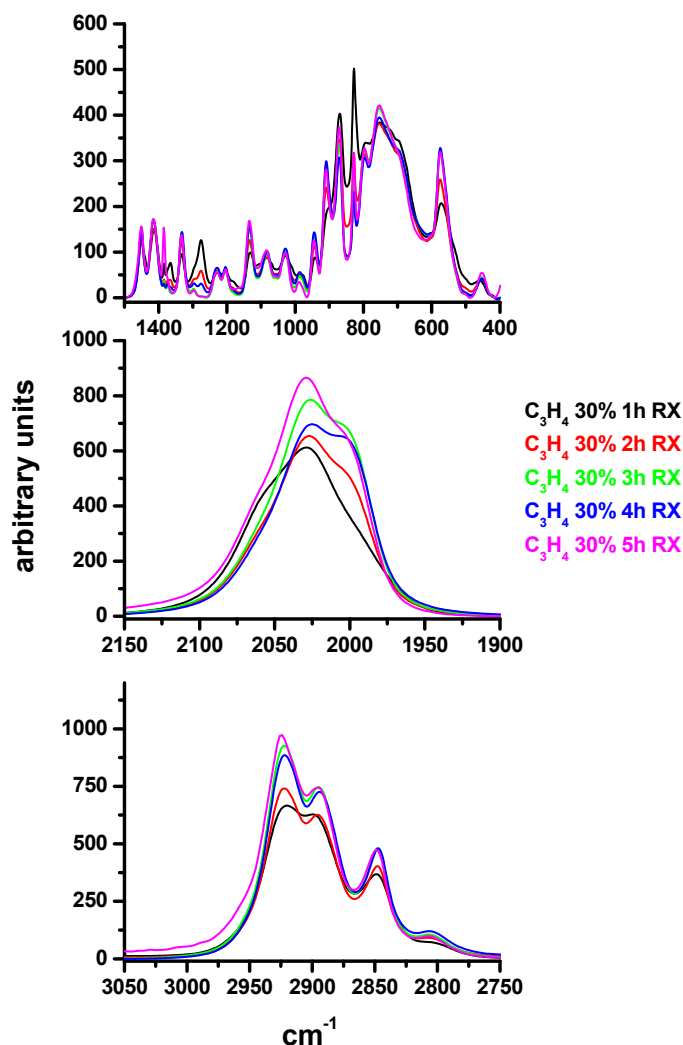
The partially overlapped bands in the 3050–2750 cm<sup>-1</sup> range can be assigned to the C-H bonds stretching signals (νC-H). The deconvolution of νC-H peaks gives signals around 2925, 2896 and 2851 cm<sup>-1</sup> as evidenced in the insert of Figure 6. In Figure 6 the IR absorption spectrum of the solid deposited from irradiation of mixtures with 30% of allene, irradiated for 5 hours is compared with those of solids obtained, in previous works [37,39], from mixtures with 10% of ethyne and 15% of ethene.



**Figure 4. IR spectra of the solids obtained from 5 h irradiation of  $\text{GeH}_4/\text{C}_3\text{H}_4$  mixtures with different  $\text{C}_3\text{H}_4$  percentage.**

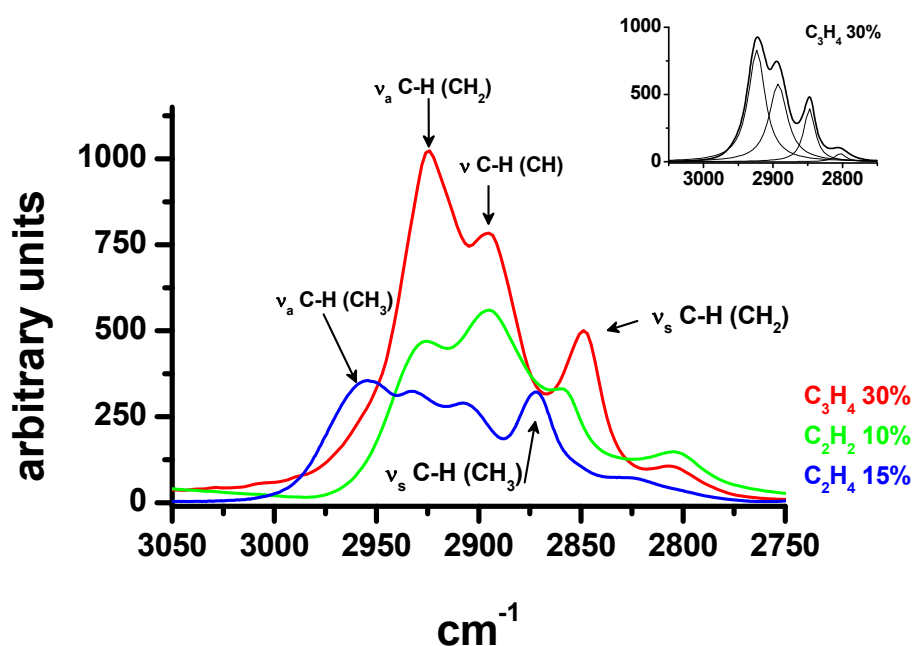
It is interesting to note that, as observed for samples deposited from ethyne, the signals around  $2953$  and  $2872\text{ cm}^{-1}$ , attributable to stretching modes of the C-H bond in the  $\text{CH}_3$  group, are absent, whereas they are clearly identifiable in IR spectra of solids obtained from radiolysis of germane/ethene mixtures.

Therefore, the materials obtained from radiolysis of allene mixtures only contain mono- and di-hydrocarbon groups and the bands at  $2851$  and  $2925\text{ cm}^{-1}$  can be attributed to the symmetrical and asymmetrical stretching vibrations of hydrogen atoms in the  $\text{CH}_2$  group, respectively, while the signal around  $2896\text{ cm}^{-1}$  to the C-H stretching mode in monohydrocarbon group[3,6,9,17,46–51]. The signal around  $2800\text{ cm}^{-1}$  is also present, but it has not been attributed yet.



**Figure 5.** IR spectra of the solids obtained from 1 to 5 h irradiation of  $\text{GeH}_4/\text{C}_3\text{H}_4$  mixtures with 30% of  $\text{C}_3\text{H}_4$ .

Moreover, while in the solid obtained from ethyne, the integrated absorption of deconvoluted CH stretching signal ( $\int \nu_{\text{CH}}$ ), is always higher than those attributed to the  $\text{CH}_2$  stretching mode ( $\int \nu_{\text{CH}_2}$ ), in the solids from allene,  $\int \nu_{\text{CH}_2} > \int \nu_{\text{CH}}$  (see Figures 4, 5 and 6). This is in agreement with the H/C ratio calculable as a difference considering the hydrogenation degree of a-Ge:H obtained from 5 hours radiolysis ( $\text{H}/\text{Ge} = 1.12$ ) [44]. In fact H/C values are between 1.65 and 1.80, for 5 hours radiolysis, when allene content ranges from 10 to 70%. Therefore it can be hypothesized that H atoms are incorporated in the solid network mainly as  $-\text{CH}_2$  groups promoting the C- $\text{sp}^3$  atoms hybridization, a polymeric-like character of the network and affecting the resulting structural order [45,52,53].



**Figure 6.** IR absorption spectra (between 3050–2750  $\text{cm}^{-1}$ ), of the solids obtained from irradiation of mixtures with 10% of ethyne, 15% of ethene and 30% of allene, irradiated for 5 hours. In the insert, the deconvoluted signals of the solid obtained from irradiation of the of 30% of allene mixture, are reported as an example.

The absence of  $\text{CH}_3$  bonding configuration is a remarkable feature and it is in agreement with the above mentioned stability to the air. In fact  $\text{CH}_3$  groups favor oxidation leading to less dense materials with inner surfaces or voids [48] which allow the oxygen penetration into the sample.

Another feature in this spectrum zone is the absence of signals, at wavenumber higher than 3000  $\text{cm}^{-1}$ , attributable to C-H stretching modes of grouping with unsaturated carbon, even if in the carbon precursor two unsaturations are present.

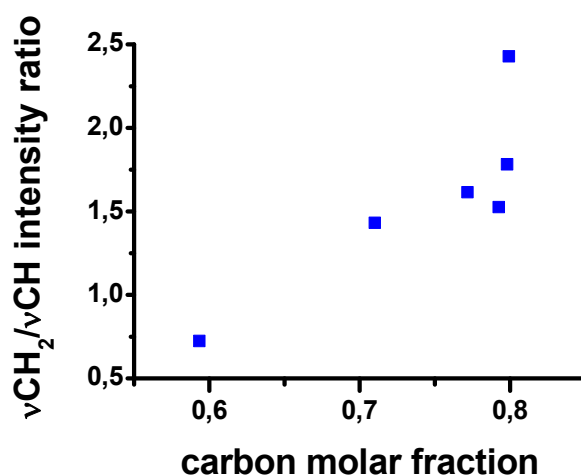
The above considerations, the elemental analysis results and the absence of allene autocondensation reactions (as above reported) indicate that polymerization reactions leading to mixed species, containing Ge-C bonds, are favored.

In the 2150–1900  $\text{cm}^{-1}$  wave number region the samples exhibit a signal resulting from partially overlapped peaks (Figures 5 and 6). Three deconvoluted bands are obtained around 1990, 2020 and 2050  $\text{cm}^{-1}$ , attributable to Ge-H bond stretching in the  $\text{GeH}_n$  ( $n = 1-3$ ) groups [40,43] but a univocal attribution is not possible. In fact in Ge-C:H alloys, a different number of neighbouring carbon atoms can be bound to Ge and the Ge- $\text{H}_n$  stretching mode can be shifted as a consequence of the higher carbon electronegativity [37,45,54]. Therefore, as reported in a previous work [39], the band around 2050  $\text{cm}^{-1}$  can be attributed to  $\text{GeH}_3$ ,  $\text{C}_2\text{GeH}_2$  or  $\text{C}_3\text{GeH}$ ; the band around 2020  $\text{cm}^{-1}$  to  $\text{GeC}_2\text{GeH}$  or  $\text{GeCCGeH}_2$  and the band around 1990  $\text{cm}^{-1}$  can be assigned to  $\text{Ge}_2\text{CGeH}$  or  $\text{Ge}_2\text{GeH}_2$ : each deconvoluted band is a sum of contributions of different groups.

In agreement with the above considerations the integrated absorption of deconvoluted signals does not exhibit a regular trend with increasing carbon content in the solids. Moreover, as it is evident



in Figure 4, a shift of the Ge-H<sub>n</sub> stretching band to lower wave numbers is observed with increasing allene percentage. These findings indicate a variation of the contribution of the different groups to each signal. In fact, it must be considered that the Ge-C bonds formation is promoted by an higher hydrocarbon percentage; moreover, a change of the Ge atoms hydrogenation degree is expected considering the increase of both CH<sub>n</sub> (n = 1, 2) stretching band intensities, (Figure 4) and the  $\int\nu\text{CH}_2/\int\nu\text{CH}$  ratio, shown in Figure 7. Therefore, less hydrogenated Ge<sub>x</sub>C<sub>y</sub>H<sub>z</sub> (x, y, z = 1–3) groups and with more C neighbouring atoms are favored.



**Figure 7. Ratio of the deconvoluted infrared stretching signals of hydrogenated carbon groups,  $\int\nu\text{CH}_2/\int\nu\text{CH}$ , of the solids obtained from 5 h irradiation of GeH<sub>4</sub>/C<sub>3</sub>H<sub>4</sub> mixtures with different percentage of C<sub>3</sub>H<sub>4</sub> as a function of carbon molar fraction.**

In the 1500–400 cm<sup>-1</sup> range the interpretation of IR spectra is difficult due to the presence of many broad and partially overlapped bands (Figures 4 and 5).

However, the GeCH<sub>n</sub> (n = 1, 2) and GeH<sub>2</sub> bending modes [3,27,29], besides Ge-C stretching and Ge-H wagging modes, are generally found in the wave number region between 500 and 900 cm<sup>-1</sup>. Moreover, rocking vibrational modes of various skeletal group systems, such as Ge-H, Ge-C, and (CH<sub>m</sub>)<sub>n</sub>-C/Ge, are expected at 1200–400 cm<sup>-1</sup> [3,6,40,49,55]. In particular, the sharp band at 570 cm<sup>-1</sup> can be attributed to the superimposed signals of Ge-C stretching and GeH wagging modes. The finding that the signal intensity increases with the solid carbon content, while a decreasing of Ge atoms hydrogenation degree is expected, as above reported, confirms the signal attribution and indicates an increase of Ge-C bonds.

### *Optical properties*

One of the most important characteristics of these materials is the optical bandgap value ( $E_{\text{opt}}$ ), i.e. the gap between the extended state in the valence and in the conduction band. The absorption spectrum in the ultraviolet-visible range is commonly used to obtain the  $E_{\text{opt}}$  value.

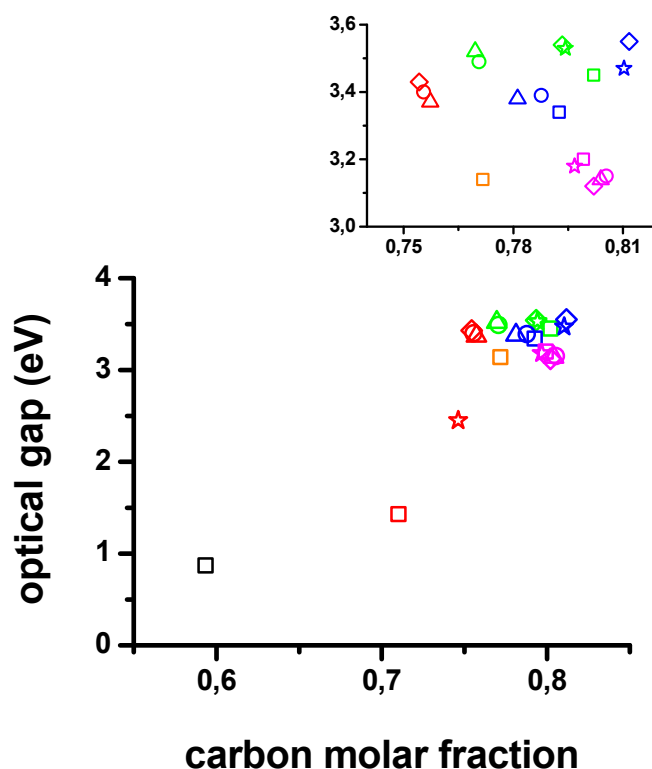
For this reason, absorption measurements have been made at photon energies between 0.5 and 7 eV for all the solids. The optical gap values have been obtained using the common procedure of

Tauc [56–57] from intercept with the x axis of the extrapolated linear part of the curve obtained by plotting  $(\alpha h\nu)^{1/2}$  against the photon energy according to:

$$(\alpha h\nu)^{1/2} = B^{1/2}(h\nu - E_{\text{opt}})$$

where  $\alpha$  is the absorption coefficient from spectrophotometric measurements,  $h$  the Planck's constant,  $\nu$  the photon frequency and  $E_{\text{opt}}$  is the optical band gap.

These measurements also allow to obtain the  $B^{1/2}$  value (so-called Tauc slope) which is considered to be a measure of the randomness of the network. Large  $B^{1/2}$  values correspond to high order and imply the existence of wider tails of localized states in energy band structures [58,59].



**Figure 8.**  $E_{\text{opt}}$  value of the solids obtained from 1 to 5 hours irradiation of  $\text{GeH}_4/\text{C}_3\text{H}_4$  mixtures with different percentage of  $\text{C}_3\text{H}_4$  is reported as a function of carbon molar fraction. In the insert only the gap values between 3.12 and 3.55 eV are shown to facilitate reading and examination. Note: colors are used to indicate allene percentage: black, red, orange, green, blue and fuchsia are used to indicate 5, 10, 20, 30, 50 and 70  $\text{C}_3\text{H}_4$  percentage, respectively.  $\Delta$ ,  $\circ$ ,  $\diamond$ ,  $\star$  and  $\square$  are used to indicate the irradiation time from 1 to 5 hours, respectively.

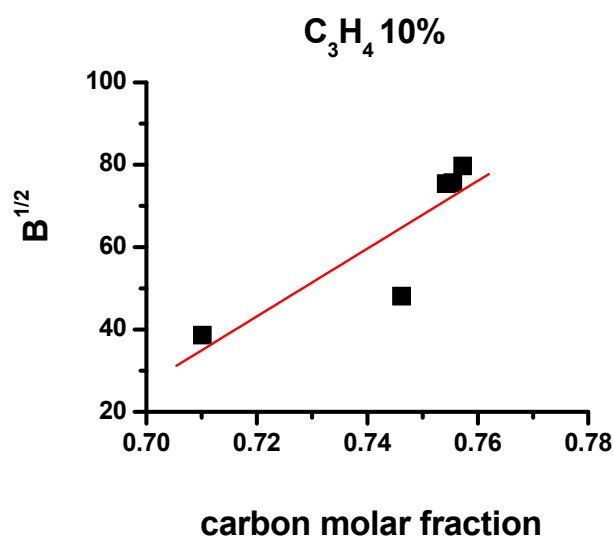
In Figure 8 the  $E_{\text{opt}}$  value of the solids obtained from 1 to 5 hours irradiation of  $\text{GeH}_4/\text{C}_3\text{H}_4$  mixtures with different percentage of  $\text{C}_3\text{H}_4$  is reported as a function of carbon molar fraction. The trend of gap values, increasing for carbon molar fraction between 0.59 and 0.75, is consistent with C  $\text{sp}^3$ -bonding configuration, in agreement with the compositional and infrared spectroscopy

results above reported and evidencing high hydrogen content and absence of any C-H stretching modes of grouping with unsaturated carbon. In fact, in a-GeC:H  $sp^3$  bonded alloys, the Ge-Ge bonds can be replaced by stronger Ge-C bonds or even stronger C-C bonds [60,61], leading to high  $E_{opt}$  values which increase with C content. For  $C/(C+Ge)$  values higher than 0.75, the  $E_{opt}$  is less influenced by the carbon molar fraction increase and values varying in a narrow range centered around 3.5 eV found. This is probably because for carbon molar fraction values higher than 0.75, the carbon incorporation affects the Ge-C and particularly the C-C bonds formation not so much as for lower values. This hypothesis is supported by IR results: in fact, the raise of Ge-C bond stretching signal (around  $570\text{ cm}^{-1}$ ) observed if solids obtained with lower allene percentage (having lower  $C/(Ge+C)$  values) are compared, is sharper with respect to that observed when comparing materials from allene percentage higher than 20%.

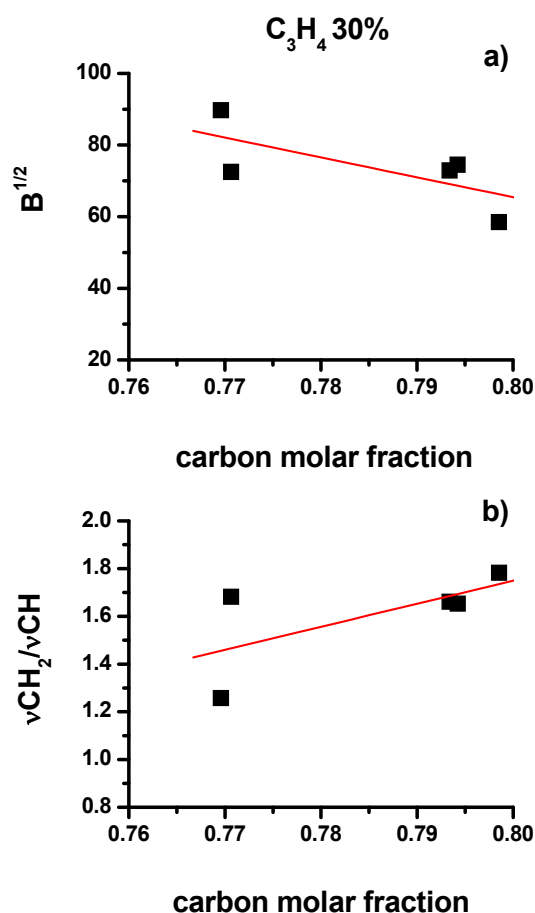
Moreover, it is interesting to note that  $E_{opt}$  values around 3.5 eV are found also starting from mixtures with very different allene percentage, thus indicating that the a-GeC:H obtained not only have close composition but also show very similar structural and optical properties.

It is interesting to compare the results obtained from 1 to 5 hours irradiation of  $GeH_4/C_3H_4$  mixtures with 10 and 30% of  $C_3H_4$  (mixtures with 50 and 70% of  $C_3H_4$  show similar trend to 30%).

In Figures 9 and 10 the  $B^{1/2}$  value of solids, obtained from 1 to 5 hours irradiation of  $GeH_4/C_3H_4$  mixtures with 10 and 30 % of  $C_3H_4$ , are reported as a function of carbon molar fraction, respectively. Figure 10 also reports the  $\int \nu CH_2 / \int \nu CH$  ratio as a function of carbon molar fraction.



**Figure 9.**  $B^{1/2}$  value of solids obtained from 1 to 5 hours irradiation of  $GeH_4/C_3H_4$  mixtures with 10% of  $C_3H_4$  as a function of carbon molar fraction.



**Figure 10.**  $B^{1/2}$  value and  $\int \nu CH_2 / \int \nu CH$  ratio of solids obtained from 1 to 5 hours irradiation of GeH<sub>4</sub>/C<sub>3</sub>H<sub>4</sub> mixtures with 30% of C<sub>3</sub>H<sub>4</sub> as a function of carbon molar fraction.

To explain the different trend of  $B^{1/2}$  with carbon molar fraction, the very different nature of the material obtained from 10 and 30 allene percentage must be considered. In fact, the  $B^{1/2}$  value can be affected by composition, atoms distribution in the material and hydrogenation degree of carbon atoms. At low C<sub>3</sub>H<sub>4</sub> percentage, the deposition probability of Ge-rich materials is higher and increases with irradiation time, as confirmed by composition results showing a reduction of carbon molar fraction (see Figure 2). As a consequence, amorphous germanium zones (a-Ge) can be formed in the solid matrix leading to lower  $E_{opt}$  and more disordered material and hence, lower  $B^{1/2}$  value. A calculation of Ge-rich and C-rich zones percentage in the materials is not possible, but Raman results show, for solids obtained with lower C<sub>3</sub>H<sub>4</sub> percentage, a weak signal due to amorphous germanium clusters, while the absence of  $sp^2$  C signals confirm the polymeric character of the material.

For higher allene percentage the a-Ge zone are sharply reduced and the  $B^{1/2}$  value mainly depends on hydrogen distribution. The  $\int \nu CH_2 / \int \nu CH$  ratio increases with carbon content (figure 10) increasing the polymeric character of the material and the disorder degree [62] leading to lower  $B^{1/2}$  values.

#### 4. Conclusion

Ge<sub>x</sub>C<sub>1-x</sub>:H alloys have been obtained by X-Ray Chemical Vapor Deposition from mixtures of GeH<sub>4</sub> with C<sub>3</sub>H<sub>4</sub>. They can be considered a randomly bound network of carbon and germanium atoms with hydrogen atoms terminating all the dangling bonds. Moreover, the IR spectra indicate that the materials obtained from radiolysis only contain mono and dihydrocarbon groups while unsaturated hydrogenated carbon moieties are absent. This finding, the elemental analysis results and the absence of allene autocondensation reactions products indicate that polymerization reactions leading to mixed species, containing Ge-C bonds, are favored.

It is remarkable that (except for allene lower than 20%) the solids exhibit composition and E<sub>opt</sub> value varying in a narrow range even starting from mixtures with allene content ranging from 20 to 70%. The high gap value can be attributed to C sp<sup>3</sup>-bonding configuration also favored by the high hydrogen solid content. The B<sup>1/2</sup> value, related to the order degree, was found to be dependent on solid composition, atoms distribution in the material and hydrogenation degree of carbon atoms.

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#### Conflict of Interest

The authors report no conflict of interests in this research.

#### References

1. Mazerolles P, Morancho R, Reynes A (1986) *Silicon, Germanium, Tin, Lead Compd* 9: 243–271.
2. Seraphin BO (1976) *Optical Properties of Solids. New Developments*; North-Holland Publishing Co.: Amsterdam, NL.
3. Drüsedau T, Andreas A, Schröder B, et al. (1994) Vibrational, optical and electronic properties of the hydrogenated amorphous germanium-carbon alloy system. *Philos Mag* 69: 1–20.
4. Saito N, Nakaaki I, Iwata H, et al. (2007) Optical and electrical properties of undoped and oxygen-doped a-GeC:H films prepared by magnetron sputtering. *Thin Solid Film* 515: 3766–3771.
5. Kumar S, Kashyap SC, Chopra KL (1998) Structure and transport properties of amorphous Ge<sub>1-x</sub>C<sub>x</sub>:H thin films obtained by activated reactive evaporation. *J Non-Cryst Solids* 101: 287.
6. Shinar J, Wu HS, Shinar R, et al. (1987). An IR, optical, and electron-spin-resonance study of as-deposit ed and annealed a-Ge<sub>1-x</sub>C<sub>x</sub>-H prepared by RF-sputtering in Ar/H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub>. *J Appl Phys* 62: 808–812.
7. Saito N, Nakaaki I, Yamaguchi T, et al. (1995) Influence of deposition conditions on the properties of a-GeC:H and a-Ge:H films prepared by rf magnetron sputtering. *Thin Solid Films* 269: 69–74.
8. Jacobsohn LG, Freire FL, Mariotto G (1998) Investigation on the chemical, structural and mechanical properties of carbon-germanium films deposited by dc-magnetron sputtering. *Diam Relat Mater* 7: 440–443.
9. Vilcarrromero J, Marques FC (1999) Hydrogen in amorphous germanium-carbon. *Thin Solid Films* 343–344: 445–448.

10. Mariotto G, Vinegoni C, Jacobsohn LG, et al. (1999) Raman spectroscopy and scanning electron microscopy investigation of annealed amorphous carbon-germanium films deposited by d.c. magnetron sputtering. *Diam Relat Mater* 8: 668–672.
11. Kumeda M, Masuda A, Shimizu T (1998) Structural studies on hydrogenated amorphous germanium-carbon films prepared by RF sputtering. *Jpn J Appl Phys* 36: 1754–1759.
12. Hu CQ, Zheng WT, Zheng B, et al. (2004) Chemical bonding of a-Ge<sub>1-x</sub>C<sub>x</sub>:H films grown by RF reactive sputtering. *Vacuum* 77: 63–68.
13. Yuan H, Williams R (1993) Synthesis by laser ablation and characterization of pure germanium-carbon alloy thin-films. *Chem Mater* 5: 479–485.
14. Booth DC, Voss KJ (1981) The optical and structural properties of CVD germanium carbide. *J Phys Colloques* 42: C4-1033–C4-1036.
15. Gazicki M. (1999) Plasma deposition of thin carbon/germanium alloy films from organogermanium compounds. *Chaos Soliton Fract*, 10: 1983–2017.
16. Kazimierski P, Tyczkowski J, Kozanecki M, et al. (2002) Transition from amorphous semiconductor to amorphous insulator in hydrogenated carbon-germanium films investigated by Raman spectroscopy. *Chem Mater* 14: 4694–4701.
17. Gazicki M, Ledzion R, Mazurczyk R, et al. (1998) Deposition and properties of germanium/carbon films deposited from tetramethylgermanium in a parallel plate RF discharge. *Thin Solid Films* 322:123–131.
18. Kazimierski P, Tyczkowski J (2003) Deposition technology of a new nanostructured material for reversible charge storage. *Surf Coat Tech* 174-175: 770–773.
19. Inagaki N, Mitsuuchi M (1984) Photoconductive films prepared by glow discharge polymerization. *J Polym Sci* 22: 301–305.
20. Szmidi J, Gazicki-Lipman M, Szymanowski H, et al. (2003) Electrophysical properties of thin germanium/carbon layers produced on silicon using organometallic radio frequency plasma enhanced chemical vapor deposition process. *Thin Solid Films* 441: 192–199.
21. Sathir RK, James WJ, Auerbach RA, et al. (1984) Synthesis of organogermanium by glow discharge polymerization. *J Appl Polym Sci* 38: 99–104.
22. Zhu JQ, Jiang CZ, Han JC, et al. (2012) Optical and electrical properties of nonstoichiometric a-Ge<sub>1-x</sub>C<sub>x</sub> films prepared by magnetron co-sputtering. *Appl Surf Sci* 258:3877–3881.
23. Mahmood A, Shah A, Castillon FF, et al. (2011) Surface analysis of GeC prepared by reactive pulsed laser deposition technique. *Curr Appl Phys* 11:547–550.
24. Schrader JS, Huguenin-Love JL, Soukup RJ, et al. (2006) Thin films of GeC deposited using a unique hollow cathode sputtering technique. *Sol Energy Mater Sol Cells* 90: 2338–2345.
25. Yashiki Y, Miyajima S, Yamada A, et al. (2006) Deposition and characterization of mu c-Ge<sub>1-x</sub>C<sub>x</sub> thin films grown by hot-wire chemical vapor deposition using organo-germane. *Thin Solid Films* 501: 202–205.
26. Hu CQ, Zheng WT, Tian HW, (2006) Effects of the chemical bonding on the optical and mechanical properties for germanium carbide films used as antireflection and protection coating of ZnS windows. *J Phys: Condens Matter* 18: 4231–4241.
27. Li YP, Li J, Wang N, et al. (2014) Optical and structural properties of co-sputtered Ge<sub>1-x</sub>C<sub>x</sub> thin films as a function of the substrate temperature. *Thin Solid Films* 551: 74–78.
28. Wu X, Zhang W, Y Lanqin, et al. (2008) The deposition and optical properties of Ge<sub>1-x</sub>C<sub>x</sub> thin film and infrared multilayer antireflection coatings. *Thin Solid Films* 516: 3189–3195.

29. Li YP, Liu Z, Zhao H, et al. (2009) Infrared transmission properties of germanium carbon thin films deposited by reactive RF magnetron sputtering. *Vacuum* 83: 965–969.
30. Saito N, Iwata H, Nakaaki I, et al. (2009) Amorphous and microcrystalline GeC:H films prepared by magnetron sputtering. *Physica Status Solidi (a)* 206: 238–242.
31. Mahmood A, Shah A, Castillon FF, et al. (2011) Surface analysis of GeC prepared by reactive pulsed laser deposition technique. *Curr Appl Phys* 11: 547–550
32. Antoniotti P, Benzi P, Castiglioni M, et al. (1992) Studies on the solid obtained from radiolysis of germane methane mixtures. *Chem Mater* 4: 717–720.
33. Benzi P, Castiglioni M, Volpe P (1994)  $\alpha$ -GeC precursors obtained by radiolysis of GeH<sub>4</sub>-hydrocarbon mixtures. *J Mater Chem* 4: 1067–1070.
34. Antoniotti P, Benzi P, Castiglioni M, et al. (1996) Radiolysis of binary systems containing germanium and carbon hydrides. *Radiat Phys Chem* 48: 457–462.
35. Benzi P, Castiglioni M, Truffa E, et al. (1996) Thin film deposition of Ge<sub>x</sub>C<sub>y</sub>H<sub>z</sub> by radiolysis of GeH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub> mixtures. *J Mater Chem* 6: 1507–1509.
36. Antoniotti P, Benzi P, Castiglioni M, et al. (1999) An experimental and theoretical study of gaseous products in the radiolysis of germane/ethylene mixtures. *Eur J Inorg Chem* 323–332.
37. Benzi P, Castiglioni M, Volpe P (2001) Characterisation and properties of amorphous nonstoichiometric Ge<sub>1-x</sub>C<sub>x</sub>:H compounds obtained from X-ray radiolysis of germane/ethylene mixtures. *Eur J Inorg Chem* 1235–1242.
38. Benzi P, Bottizzo E, Operti L, et al. (2002) Amorphous germanium carbides by radiolysis-CVD of germane/ethyne systems: Preparation and reaction mechanisms. *Chem Mater* 14: 2506–2513.
39. Benzi P, Bottizzo E, Operti L, et al. (2004) Characterization and properties of amorphous nonstoichiometric Ge<sub>1-x</sub>C<sub>x</sub>:H compounds obtained by radiolysis-CVD of germane/ethyne systems. *Chem Mater* 16: 1068–1074.
40. Benzi P, Bottizzo E, Demaria C (2006) Characterization and properties of Ge<sub>1-x</sub>C<sub>x</sub>:H compounds obtained by X-ray CVD of germane/ethyne systems: Effect of the irradiation dose. *Chem Vapor Depos* 12: 25–32.
41. Benzi P, Bottizzo E, Demaria C, et al. (2007) Amorphous nonstoichiometric Ge<sub>1-x</sub>C<sub>x</sub>:H compounds obtained by radiolysis-chemical vapor deposition of germane/ethyne or germane/allene systems: A bonding and microstructure investigation performed by x-ray photoelectron spectroscopy and Raman spectroscopy. *J Appl Phys* 101: 124906.
42. Demaria C, Benzi P, Arrais A, et al. (2013) Growth and thermal annealing of amorphous germanium carbide obtained by X-ray chemical vapor deposition. *J Mat Sci* 48: 6357–6366.
43. Arrais A, Benzi P, Bottizzo E, et al. (2007) Characterization of hydrogenated amorphous germanium compounds obtained by x-ray chemical vapor deposition of germane: Effect of the irradiation dose on optical parameters and structural order. *J Appl Phys* 102:104905.
44. Arrais A, Benzi P, Bottizzo E, et al. (2009) Correlations among hydrogen bonding configuration, structural order and optical coefficients in hydrogenated amorphous germanium obtained by x-ray-activated chemical vapour deposition. *J Phys D Appl Phys* 42:105406.
45. Chew K, Rusli, Yoon SF, et al. (2002) Hydrogenated amorphous silicon carbide deposition using electron cyclotron resonance chemical vapor deposition under high microwave power and strong hydrogen dilution. *J Appl Phys* 92: 2937–2941.

46. Gazicki M, Schalko J, Olcaytug F, et al. (1994) Study on electromagnetron for plasma polymerization. 2. Magnetic-field enhanced radio-frequency plasma deposition of organogermanium films from tetraethylgermanium. *J Vac Sci Technol A* 12 345–353
47. Taga K, Hamada S, Fukui H, et al. (2002) Vibrational spectra and density functional study of propylgermane. *J Mol Struct* 610: 85–97.
48. Rübel H, Schröder B, Fuhs, W, et al. (1987) IR spectroscopy and structure of RF magnetron sputtered a-SiC-H films. *Phys Stat Sol* 139: 131–143
49. Cardona M (1983) Vibrational Spectra of Hydrogen in Silicon and Germanium. *Phys Stat Sol* 118: 463–481.
50. Bellamy LJ (1975) *The Infrared Spectra of Complex Molecules*, 3rd ed. Chapman and Hall, London 13–36.
51. Schrader B (1995) *Infrared and Raman Spectroscopy*, VCH, Weinheim, 192–195.
52. Gharbi R, Fathallah M, Alzaied N, et al. (2008) Hydrogen and nitrogen effects on optical and structural properties of amorphous carbon. *Mat Sci Eng C* 28: 795–798.
53. Robertson J (1986) Amorphous-carbon. *Adv Phys* 35: 317–374.
54. Akaoglu B, Sel K, Atilgan I, et al. (2008) Carbon content influence on the optical constants of hydrogenated amorphous silicon carbon alloys. *Opt Mat* 30: 1257–1267.
55. Lucovsky G (1985) Local bonding of hydrogen in a-Si H, a-Ge H and a-Si, Ge H alloy-films. *J Non-Cryst Solids* 76, 173–186.
56. Ley L (1984) *The Physic of Hydrogenated Amorphous Silicon II*, Springer-Verlag, New York, Chap. 3, 61–161.
57. Tauc J (1974) *Amorphous and Liquid Semiconductors*, Plenum, London and New York Chap. 4, 159–220.
58. Mott NF, Davis EA (1979) *Electronic Process in Non-Crystalline Materials*, 2nd ed. Clarendon Press. Oxford, 287–318.
59. Masuda A, Kumeda M, Shimizu T (1991) Relationship between photodarkening and light-induced ESR in amorphous Ge-S films alloyed with lead. *Jpn J Appl Phys* 30: L1075.
60. Lide DR (1997–1998) *CRC Handbook of Chemistry and Physics*, 78th ed. CRC Press, Boca Raton and New York.
61. Robertson J (1992) The electronic and atomic structure of hydrogenated amorphous Si-C alloys. *Phil Mag B* 66: 615–638.
62. Mihailova T, Toneva A (1995) Effect of the gas pressure during deposition on the optical properties of HOMOCVD a-Si:H thin films. *Sol Energ Mat Sol C* 36: 1–9.

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